



## Selective oxidation of 5-hydroxymethyl furfural over non-precious metal heterogeneous catalysts



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### ABSTRACT

An alternative synthesis of 2,5-furandicarboxylic acid (FDCA) was carried out by oxidation of 5-hydroxy-2-methyl furfural (HMF) in aqueous medium. The reaction occurred in presence of non-precious metal ( $Mn_xFe_y$ ) mixed oxide catalyst. The effect of various reaction parameters such as nature and amount of base, reaction temperature, oxygen pressure, catalyst composition were investigated in order to quantitatively produce FDCA. The catalytic behavior of the mixed oxide catalyst was assigned to an optimal Mn/Fe ratio of 3/1, where a mixture of Mn(III) and Mn(IV) coexists with a hematite phase. The synergetic cooperation of these phases allowed the efficient oxidation of FFCA to FDCA. The humins species formed by HMF degradation exhibited a negative effect over the catalytic activity of Mn/Fe mixed oxide, while the chlorine resulted after the pH modification had no influence upon the catalytic oxidation.

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## 1. Introduction

Depletion of fossil resources has generated serious concerns during the past decade. Currently, production of both energy and chemicals requires alternative resources and a severe environmental control [1]. A potential solution could be the use of renewable resources. Since renewable resources like biomass already contain oxygen, such a strategy is mostly feasible for the production of oxygen-containing compounds [2].

Following this strategy, alternative to polyethylene terephthalate (PET) can be economically produced from the oxidation of 5-Hydroxymethyl-2-furfural (HMF). HMF represents an important, versatile and available primary renewable platform molecule that is structurally found into numerous pharmaceuticals, antifungal agents, as well as polymers, whose synthesis is attempted starting from carbohydrates such as fructose, glucose, cellulose etc [3–9]. Then, 2,5-Furandicarboxylic acid (FDCA) is a promising biomass-derived chemical building block with a great market potential. It is considered one of the top added-value chemicals among biomass [10] merely because it may conveniently replace terephthalic acid in PET [11] manufacture. The classic synthesis of FDCA from HMF

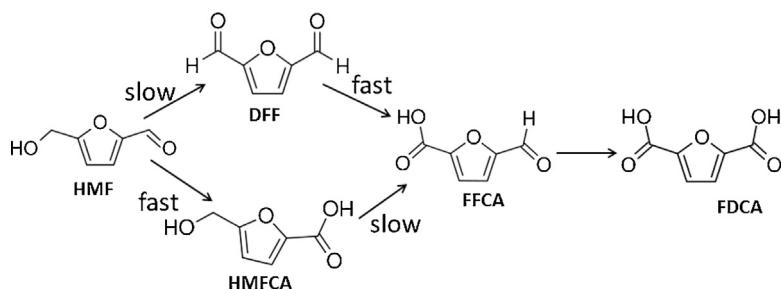
usually involves high pressure and temperature, metal salts and organic solvents [12–16] which render the process to be quite expensive and polluting. Therefore, a new greener route for the synthesis of FDCA may be designed in the presence of versatile heterogeneous catalysts.

The literature survey for the oxidation of HMF to FDCA indicated that this reaction has been performed using stoichiometric amounts of oxidants and expensive catalytic systems containing noble metals such as Pt [17–22], Pd [23–26], Au [27–32], Ru [33], or their alloys [34–41]. In addition, the presence of a base is crucial in order to facilitate the desorption of the resulted acid from the catalytic surface. However, the presence of the base can lead to a gradual degradation of HMF [32,42–44]. Other reports claim a high selectivity to FDCA without the addition of any base, [45,46] when TBHP is used as oxidizing agent and  $CuCl_2$  as catalyst (selectivity of 48% after 48 h [46]).

On the other hand, manganese oxides including bulk and supported  $MnO_2$ ,  $Mn_2O_3$  and  $Mn_3O_4$  on silica, alumina, titania and zirconia were reported as efficient cheaper alternatives in environmental oxidation catalysis. These oxides are known to exhibit high activity in hydrocarbon and VOC catalytic combustion, oxidation of HMF to DFF [47], as well as other oxidation reactions [48,49]. Their catalytic behavior is related to both redox capabilities and acid-base properties, and as it resulted from the work of Liu et al. [47] the promotion of the HMF oxidation depends on the oxidation state of manganese and its surroundings.

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**Scheme 1.** Reaction pathways in oxidation of HMF to FDCA (DFF: 2-diformyl furan; FFCA: 5-formyl-2-furancarboxylic acid; HMFCA: 5-hydroxymethyl-2-furancarboxylic acid).

Herein, we report an environmentally benign and safe alternative for the synthesis of FDCA (Scheme 1). The oxidation of HMF was carried out under mild aqueous conditions, using Mn/Fe mixed oxides as heterogeneous catalysts.

Mn/Fe mixed oxides in 1:3, 1:1 and 3:1 atomic ratios, respectively, were prepared by co-precipitation method. For comparison purposes, pure Mn and Fe oxides were also prepared following the same procedure. The obtained catalysts were denoted MnX/Fe(1-X), where X=0.75, 0.50, 0.25.

## 2. Experimental

All reagents were of analytical purity: 5- hydroxymethyl-2-furfural (HMF, Sigma–Aldrich 99%), 5-formyl-2-furancarboxylic acid (FFCA, Sigma–Aldrich), 2,5-furandicarboxylic acid (FDCA, Sigma–Aldrich 97%), diformyl furan (DFF, Sigma–Aldrich 97%), He (purity 5.0, Linde), CO<sub>2</sub> (Linde Romania), NH<sub>3</sub> (Siad Romania), O<sub>2</sub> (purity 5.0, Linde Romania), Mn(NO<sub>3</sub>)<sub>2</sub> hexahydrate (Sigma–Aldrich), Al(NO<sub>3</sub>)<sub>3</sub> nonahydrate (Fluka 98%), Fe (NO<sub>3</sub>)<sub>3</sub> nonahydrate (Sigma–Aldrich ≥98%), Fe<sub>2</sub>O<sub>3</sub> (Sigma–Aldrich), Mn(CH<sub>3</sub>COO)<sub>2</sub> tetrahydrate (Fluka ≥99%).

### 2.1. Catalysts synthesis

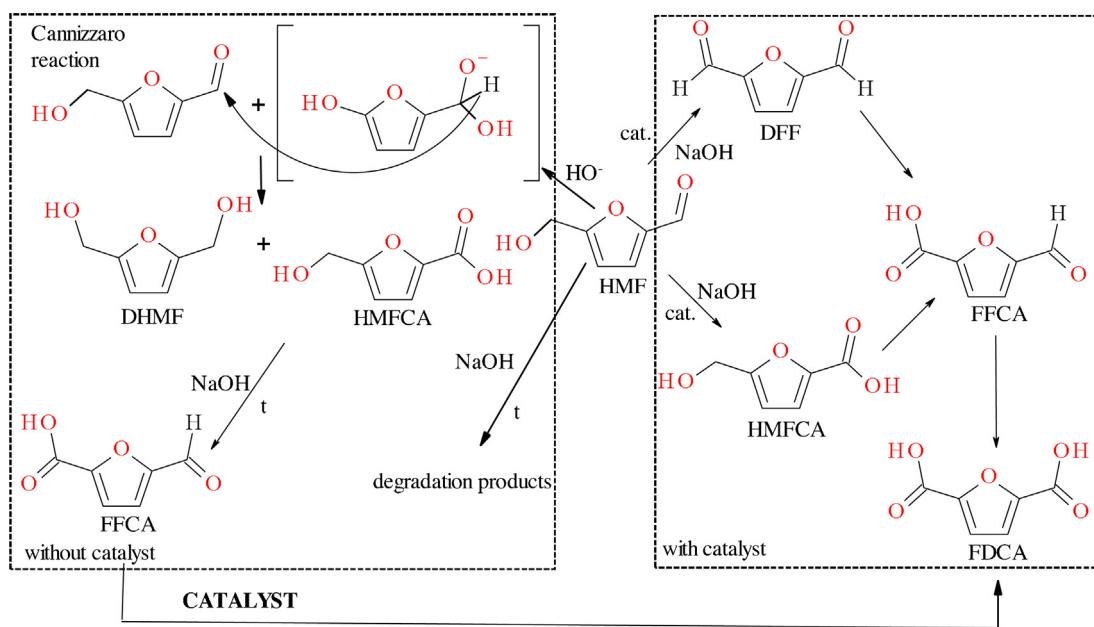
Mn/Fe mixed oxides with molar ratios varying from 1:3, 1:1, and 3:1, respectively, were prepared by co-precipitation method. The preparation procedure started from an aqueous solution of manganese nitrate and iron nitrate, containing the amounts corresponding to the above molar ratios (e.g. for the catalyst Mn0.75/Fe0.25, the calculated amount were 53.7 g (0.3 mol) Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 40.4 g (0.1 mol) Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) that were pre-mixed. To this solution, at room temperature, an appropriate volume of solutions of NaOH or Na<sub>2</sub>CO<sub>3</sub> (1.5 M) were added in order to generate a pH of 9–10. The resulted precipitates were aged overnight at 75 °C under stirring. The final precipitates were filtered, thoroughly washed until pH 7 and dried overnight at 100 °C in an oven. The calcination step has been accomplished at 460 °C for 5 h in air atmosphere. Separately, Mn<sub>2</sub>O<sub>3</sub> was prepared by the following method: 2 g of manganese acetate were added into a beaker containing 200 mL of bidistilled water. A sodium hydroxide solution (0.2 M) was added dropwise until a pH 10 was reached. Then the precipitate was aged for 1 h at 80–90 °C and then left overnight at room temperature under stirring. The brown slurry was filtrated and washed with deionized water, then dried overnight at 100 °C and calcined at 460 °C for 5 h in air atmosphere. Fe<sub>2</sub>O<sub>3</sub> was prepared mixing solutions of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and NaOH in a molar ratio of 1:3, where that containing sodium hydroxide was dropwise added to that containing iron nitrate under vigorous stirring, until a pH of 9 has been reached. After the addition of NaOH the stirring was continued for another 1 h. The precipitate was then filtered out and washed with deionized water until pH 7, then dried for 16 h at 100 °C, and calcined for 5 h at 460 °C.

### 2.2. Catalysts characterization

The samples have been investigated using different characterization techniques like powder X-ray diffraction, temperature programmed reduction analysis, XPS, Raman, and textural analysis. The XRD patterns were recorded using a Shimadzu 7000 powder diffractometer which used the Cu K $\alpha$  radiation (wavelength 1.54184 Å). The patterns were collected in the range 2 $\theta$  from 5 to 80° in steps of 0.02° 2 $\theta$ /s. The CO<sub>2</sub>-TPD measurements were carried out using AutoChem II 2920 station equipped with a TCD detector working at 250 °C. The samples (30–50 mg), placed in a U-shaped quartz reactor with an inner diameter of 0.5 cm, were pre-treated under He atmosphere at 100 °C for 1 h, and then exposed to a flow of 30 mL min<sup>-1</sup> CO<sub>2</sub> for 1 h. After that, the sample was purged with a flow of He (100 mL min<sup>-1</sup>) for 20 min at 20 °C in order to remove the weakly adsorbed species. TPD experiments were then started, with a heating rate of 10 °C min<sup>-1</sup> until 850 °C. The chemical analysis of the diluted post- reaction mixtures has been performed using a Perkin Elmer ELAN 6000 spectrophotometer with cross-flow nebulizer and argon plasma. To perform the quantification of carbon, nitrogen and hydrogen in the samples, the materials were also characterized by combustion elemental analysis using a Eurovector analyzer from Shimadzu. The textural measurements used the adsorption–desorption isotherms collected with N<sub>2</sub> at –196 °C on a Micromeritics ASAP 2010 sorption analyzer. Before the analysis the catalysts were outgassed at 200 °C in vacuum. The surface areas have been obtained using BET equation. Surface analysis was performed by X-ray photoelectron spectroscopy (XPS) carried out on PHI Quantera equipment with a base pressure in the analysis chamber of 1.3 × 10<sup>–12</sup> bar. The X-ray source was monochromatized Al K $\alpha$  radiation (1486.6 eV) and the overall energy resolution is estimated at 0.6 eV by the full width at half-maximum (FWHM) of the Au4f<sub>7/2</sub> photoelectron line (84 eV). The unavoidable charging effect was minimized by using a dual beam (electrons and Ar ions) as neutralizer and the spectra were calibrated using the C1s line (BE = 284.8 eV) of the adsorbed hydrocarbon on the sample surface (C–C or (CH)<sub>n</sub> bonding). As this spectrum was recorded at the start and the end of each experiment the energy calibration during experiments was reliable. Raman spectroscopy was performed using a Horiba spectrometer, equipped with a He–Ne ( $\lambda$  = 633 nm) laser. The spectra were recorded in the 200–4000 cm<sup>-1</sup> range.

### 2.3. Catalytic reactions

Catalytic experiments were performed under vigorous stirring in a stainless steel autoclave (HEL Instruments) at temperature (90 °C) following two strategies: (i) in the *one-pot reaction conditions*: 1 mmol of substrate (HMF), 10 mL of MiliQ water, 0.05 g of catalyst and sodium hydroxide in a molar ratio to the substrate of 1:4 were stirred in an autoclave pressurized at 8 bars. (ii) in the *two-steps reaction conditions*: firstly, 1 mmol of substrate (HMF), 10 mL of MiliQ water, and 4 mmoles sodium hydroxide were heated for



**Scheme 2.** Reaction pathways for the oxidation of HMF in the presence of NaOH without and with catalysts.

30 min at 90 °C. The acidification post-treatment was carried out with HCl until a pH 1 and was followed by the filtration of the precipitate. Before the second step, the filtrate was brought back to pH 5 with NaOH. Then, the filtrate was transferred in an autoclave and mixed with 0.05 g of catalyst and 2 mmoles NaOH were added 5 mL water. The autoclave was pressurized at 8 bars O<sub>2</sub> and heated at 90 °C for 24 h. After ending HMF oxidation and filtering off the catalyst, the mother liquor was diluted 5 times and the products were analyzed by high- performance liquid chromatography (HPLC), on a Thermo Scientific Accela 600 device equipped with a UV-vis detector and a Rezex-ROA H<sup>+</sup> column. 5-Hydroxymethyl furfural (HMF), diformyl furan (DFF), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), 5-formyl-2-furancarboxylic acid (FFCA) and 2,5-furandicarboxylic acid (FDCA) were used as standards. A maximum of absorption was found for FDCA and HMFCA at  $\lambda = 260$  nm and for HMF, FFCA and DFF at  $\lambda = 285$  nm. The mobile phase consisted of 0.05 N H<sub>2</sub>SO<sub>4</sub>, at a flow rate of 0.5 mL/min, and the analysis was carried out at 40 °C, using a two channels-detection (260 nm and 285 nm) and an injection volume of 3  $\mu$ L.

### 3. Results and discussion

Previous reports associated the oxidation of HMF to FDCA with the presence of a catalyst. In the absence of a catalyst, except the degradation products of HMF, no other species were detected as oxidizing intermediate, as already reported [19,34]. According to our blank experiments, the reaction occurs even in the absence of any catalyst (Table 1). Thus, working with a mixture containing a molar ratio HMF:NaOH of 1:8 at an oxygen pressure of 8 bars (as oxidizing agent), after only 30 min, at 90 °C, we obtained a selectivity of 7% to FDCA at 94% conversion of HMF. Under the same reaction conditions, after 8 h, the selectivity increased to 17% and after 24 h to 21% (Table 1, entries 4 and 5). In addition, the oxidation took place in the absence of oxygen pressure (air, atmospheric pressure) leading after 24 h to a conversion of 99 % and selectivity of 5% to FDCA (Table 1, entry 6). Furthermore, experiments carried out in inert atmosphere (nitrogen) after all the substrates were purged with nitrogen for 4 h led only to HMFCA and DHMF, which are both products of a Cannizzaro disproportionation reaction of HMF [50].

**Table 1**  
Blank transformations of HMF under basic conditions.

Entry	Reaction time (h)	C (%)	S <sub>FDCA</sub> (%) <sup>b</sup>	S <sub>FFCA</sub> (%) <sup>b</sup>	Yields <sub>FDCA</sub> (%)
1.	0.5	94	7	93	n.d.
2.	3	98	11	89	8
3.	6	99	14	86	10
4.	8	99	17	83	12
5.	24	99	21	79	15
6.	24 <sup>a</sup>	99	5	95	n.d.

Reaction conditions: 1 mmol substrate (HMF), 8 mmoles NaOH, water 10 mL, temperature 90 °C, oxygen pressure 8 bars;

<sup>a</sup> Reaction performed in air at atmosphere pressure. A carbon mass balance of 80–90% was obtained, because of the degradation of HMF.

<sup>b</sup> The selectivity was calculated from HPLC analysis, using calibration curves. C = conversion, S = selectivity.

The effect of the Brønsted base onto the conversion of HMF and the selectivity to FDCA was revisited in experiments without any catalyst (Table 2). Increasing the sodium hydroxide concentration from 1 to 12 m moles led to an increase of the substrate conversion from 6 to 99%. An increase of the selectivity to FDCA from 2% to 23% was also measured in these conditions. This behavior can also be assigned to the Cannizzaro disproportionation reaction of HMF that is initiated in presence of the base [50]. The increase of the temperature led to further autoxidation of 2,5-dihydroxymethylfurfural (DHMF) and HMFCA (produced from the Cannizzaro reaction) to FFCA [14,51] (Scheme 2). Under these conditions the role of the base seems to be more important than the nature of the oxidizing catalyst or oxidizing agent.

Overall, these results suggest that: (i) the first step of the oxidation, i.e., from HMF to FFCA (Scheme 1), can easily be performed in absence of any catalyst, but requires the presence of a Brønsted base (detailed characterization data (NMR, FTIR) of the obtained FFCA are presented in Supplementary Information), and ii) further oxidation of FFCA to FDCA is limited to 21% in the absence of the catalyst. Noteworthy, a series of tests in the presence of oxygen and NaOH using commercial FFCA as substrate led to similar results with those starting from HMF, namely, to a conversion of around 19% (Table 3).

On this basis we may assume that the catalyst plays an important role only for the oxidation of FFCA to FDCA. Indeed, the same

**Table 2**

Influence of the amount of the base over HMF transformation in the absence of catalyst.

Entry	HMF:NaOHmolar ratio	C%	S <sub>FDCA</sub> (%)	S <sub>HMFCA</sub> (%)	S <sub>FFCA</sub> (%)	S <sub>DFF</sub> (%)	Yields <sub>FDCA</sub> (%)
1.	1:1	6	2	0	54	44	n.d.
2.	1:2	29	8	0	91	1	n.d.
3.	1:4	79	12	0	88	0	7
4.	1:8	99	21	0	79	0	15
5.	1:12	99	23	0	77	0	16

Reaction conditions: 1 mmol substrate (HMF), oxygen pressure 8 bars, water 10 mL, temperature 90 °C, 24 h. A carbon mass balance of 80–90% was obtained, because of the degradation of HMF. C = conversion, S = selectivity.

**Table 3**

Oxidation of commercial FFCA in different conditions.

Entry	Catalyst	P <sub>O<sub>2</sub></sub> (bar)	C (%)	S <sub>FDCA</sub> (%)
1.	–	–	15	100
2.	–	8	19	100
3.	Mn0.75/Fe0.25 <sup>a</sup>	–	64	100
4.	Mn0.75/Fe0.25 <sup>a</sup>	8	99	100

Reaction conditions: 0.25 mmol substrate (FFCA), molar ratio FFCA:NaOH 1:2, water 5 mL, temperature 90 °C.

<sup>a</sup> 12 mg catalyst, C = conversion, S = selectivity.

reaction performed in the presence of the Mn0.75/Fe0.25 catalyst starting from a mixture of FFCA:NaOH = 1:2 at 90 °C in air, led to a conversion of 64%. Replacing air with O<sub>2</sub> and raising the pressure at 8 bars significantly increased the conversion of FFCA to FDCA up to 99% (Table 3, entries 3 and 4).

To our surprise, the one-pot oxidation of HMF in the presence of the base and oxygen using the same Mn0.75/Fe0.25 catalyst, resulted in a poorer selectivity in FDCA compared to the case of the reaction started from FFCA (32%) (Table 4). As it can be observed in Table 4 both the reaction parameters and the catalysts composition influence the catalytic activity. Higher temperatures and an increase of the manganese-to-iron ratio favor the oxidation of FFCA to FDCA. The obtained results suggest that the oxidation of HMF over Mn/Fe catalysts merely occurs via the DFF intermediate (Table 4, entries 4 and 5). Taking into consideration that the HMF oxidation to DFF is rather slow as compared to HMF oxidation to HMFCA, we can assume that the Mn/Fe catalyst preferentially oxidize the hydroxyl group in the detriment of the carbonyl one. Complementary information offers the study of Duan et al. [47] using magnetic Fe<sub>3</sub>O<sub>4</sub> supported Mn<sub>3</sub>O<sub>4</sub> nanoparticles. The comparison of the two systems indicates that Mn<sub>3</sub>O<sub>4</sub> is a very good candidate for the oxidation of HMF to DFF. On the contrary, the mixed oxide Mn0.75/Fe0.25 catalyst is capable to continue the oxidation to FFCA. Another advantage of this system is that it allows working in water as solvent.

The characterization of the spent catalyst after the one-pot reaction indicated changes compared to the fresh catalyst. Both Raman and XPS characterization revealed blocking of the surface by carbon-based products. The new peak at 286.4 eV (red) observed for the spent Mn0.75/Fe0.25 catalyst is assigned to the binding energy of carbon in O–C–O species, most probably resulted from HMF degradation (Fig. 1). The Raman spectra of the spent catalyst also revealed the presence at the surface of material of new

**Table 5**

Comparative conversions of FFCA to FDCA and surface areas using mixed oxides with different Mn/Fe ratios and the corresponding parent oxides.

Entry	Catalyst	Conversion <sup>a</sup> (%)	S <sub>BET</sub> (m <sup>2</sup> · g <sup>-1</sup> )
1.	Mn0.75/Fe0.25	90	102
2.	Mn0.5/Fe0.5	27	58
3.	Mn0.25/Fe0.75	5	27
4.	Mn <sub>2</sub> O <sub>3</sub>	45	202
5.	Fe <sub>2</sub> O <sub>3</sub>	3	12

<sup>a</sup> Two steps procedure reaction conditions: 1-step: 1 mmol of substrate (FFCA), 10 mL of MiliQ water, and 4 mmol NaOH, 30 min at 90 °C. Post-treatment: acidification until pH 1 with HCl. Filtration of the precipitate. Before step 2, the filtrate was brought back to pH 5 with NaOH; 2-step: The filtrate was transferred in an autoclave together with 0.05 g of catalyst, 2 mmol NaOH, 8 bars O<sub>2</sub> for 24 h at 90 °C.

carbon-based products, which contain mostly in composition sp<sup>2</sup> aromatic C.

The catalyst surface blockage by HMF degradation products was also confirmed by additional experiments. Thus, the addition of the catalyst to a non-purified FFCA solution separated from the oxidation of HMF in the presence of NaOH and O<sub>2</sub> (8 bars) led to a conversion of 32% in FDCA. Based on these results and with the scope to collect more evidences on the deactivation effect of the HMF degradation products, we changed the strategy and adopted the following two-steps protocol: (i) the non-catalytic oxidation of HMF to FFCA followed by a post-treatment consisting in a change of pH from 10 to 1. The acidification with HCl led to small amounts of a black solid precipitate that was separated by filtration. Both Raman and elemental analysis of the black precipitate indicated a composition corresponding to humins species (see Supplementary Informations), as observed also by Albonetti et al. [32]; (ii) the catalytic oxidation of the separated solution containing only FFCA under oxygen pressure (8 bars) and base. Under these conditions the conversion to FDCA reached 90% after 24 h, proving the catalyst efficiency (Table 5, entry 1).

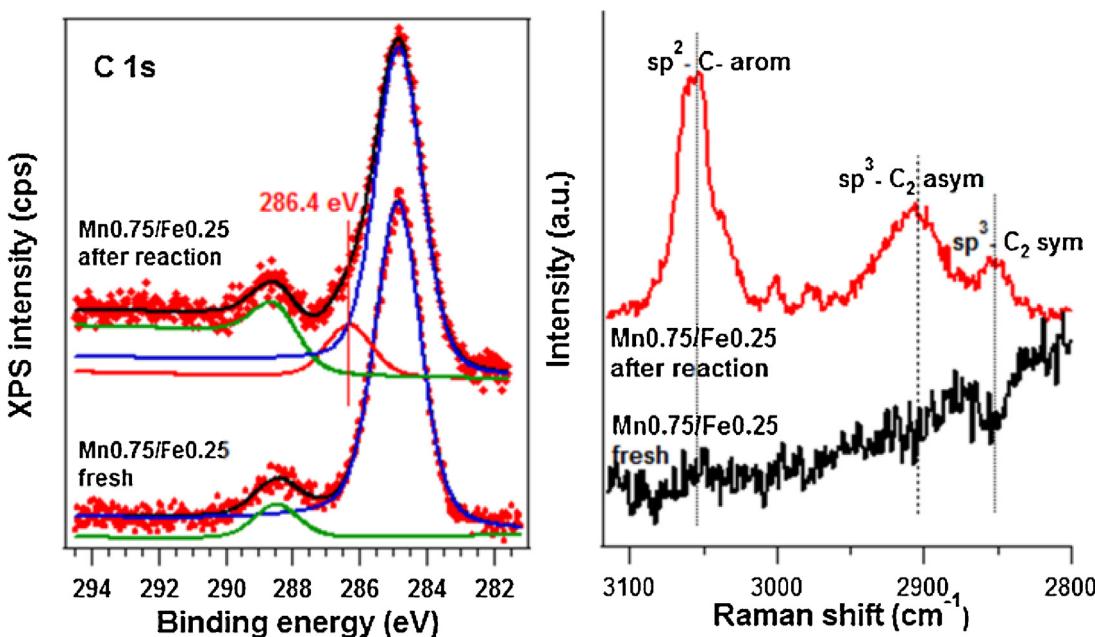
Before the second reaction step, the change of pH from 1 to 5 was achieved adding NaOH (0.5 M), thus resulting NaCl in the solution. To clarify the role of NaCl in the catalytic conversion of FFCA to FDCA, a mixture of commercial FFCA:NaOH = 1:2 was reacted in the presence of Mn0.75/Fe0.25 catalyst and NaCl (2 eq.) at 90 °C and O<sub>2</sub> (8 bars). No modification of FFCA conversion (99%) was observed, compared with the reaction performed in absence of NaCl, meaning that NaCl has no effect on the catalyst activity/stability. This is confirmed by the XPS analysis of the spent catalyst which contained in the spectra no characteristic binding energies for Cl<sup>–</sup> species.

**Table 4**

One-pot reaction of HMF oxidation over different catalyst.

Entry	Catalyst	HMF:NaOHmolar ratio	T (°C)	C%	S <sub>FDCA</sub> (%)	S <sub>HMFCA</sub> (%)	S <sub>FFCA</sub> (%)	S <sub>DFF</sub> (%)
1.	Mn0.75/Fe0.25	NaOH (1:4)	75	79	12	0	88	0
2.	Mn0.75/Fe0.25	NaOH (1:4)	90	93	32	0	68	0
3.	Mn0.75/Fe0.25	Na <sub>2</sub> CO <sub>3</sub> (1:8)	90	21	9	0	91	0
4.	Mn0.50/Fe0.50	NaOH (1:4)	90	5	0	12	0	88
5.	Mn0.25/Fe0.75	NaOH (1:4)	90	2	0	10	0	90

Reaction conditions: 1 mmol substrate (HMF), water 10 mL, 8 bars O<sub>2</sub>, 0.05 g catalyst, 24 h. A carbon mass balance of 80–90% was obtained, because of the degradation of HMF. C = conversion, S = selectivity.



**Fig. 1.** XPS and Raman spectra of Mn0.75/Fe0.25 catalysts before and after one-pot reaction starting from HMF (the new peak at 286.4 eV (red) is assigned to binding energy of carbon in O-C-O species). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The catalyst stability was checked from recycling tests. No change in the catalytic activity and selectivity has been evidenced after three successive cycles. After each cycle, the catalyst was separated by centrifugation, washed with water and dried at 60 °C for 2 h. The stability of the catalyst was also confirmed by XRD and XPS results, which showed no changes in the structure of the recycled catalyst as compared to the fresh one (see Supplementary Information) (see Fig. S2 from Supplementary information). The possible leaching of manganese or iron in the reaction mixture during the catalytic tests was analyzed by the ICP-OES technique. Thus, after filtering off the catalyst, 2 mL of the reaction mixture were sampled and diluted 5 times with ultrapure water. The results did not show any notable leaching of manganese (less than 0.05 wt.%) or iron (less than 0.18 wt.%), confirming the catalysts stability under the reaction conditions. With the same scope, the solution separated after filtering off the catalyst was maintained under the same reaction conditions (8 bars O<sub>2</sub> at 90 °C) for another 24 h. No modification of conversion or selectivity was observed, proving that, indeed, the leached species are not catalytically active in the oxidation of FFCA to FDCA.

**Table 5** presents the comparative behavior of mixed oxides with different Mn/Fe ratios and pure Mn<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> oxides for the oxidation of FFCA to FDCA.

The higher conversion corresponded to a Mn/Fe ratio of 3/1 and it decreased with the increase in the Fe content (the ratio of 1/3). The very poor activity of Fe compared to Mn is also visible when comparing the activity of Mn<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>. However, a strong synergistic effect was evidenced when the two metals were mixed by co-precipitation.

X-ray diffraction patterns of the MnX/Fe(1-X) mixed oxides are shown in **Fig. 2**. They indicate that in the most active catalyst (Mn0.75/Fe 0.25) predominates a bixbyite-Mn<sub>2</sub>O<sub>3</sub> phase (PDF card 00-041-1442) that coexists with hematite (Fe<sub>2</sub>O<sub>3</sub>) (PDF card 00-033-0664) and MnO<sub>2</sub> (PDF card 00-044-0141) phases. However, the bixbyite- Mn<sub>2</sub>O<sub>3</sub> phase was not detected in the other investigated catalysts. The Mn0.5/Fe 0.5 catalyst (27% conversion) exhibited only the characteristic patterns of MnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>, while in the pattern of Mn0.25/Fe 0.75 catalyst (5% conversion) the manganese compounds were silent. For the pure manganese and iron oxides, the

XRD patterns included only diffraction lines assigned to Mn<sub>2</sub>O<sub>3</sub> (PDF card 00-041-1442) and Fe<sub>2</sub>O<sub>3</sub> (PDF card 00-033-0664).

Based on these results we may assume that to complete the FFCA oxidation is necessary the cooperation of two manganese phases and one of iron (hematite). Despite the literature reports [52] stressing on the role of individual Mn<sub>2</sub>O<sub>3</sub> these results demonstrate that the coexistence of the manganese in both (III) and (IV) oxidation states is important.

Recent achievements emphasized that the surface basicity improve the catalyst's oxidant strength [53]. In order to confirm this, the catalysts basicity has been determined and correlated to the catalytic performances.

**Fig. 3** presents the CO<sub>2</sub>-TPD profiles of the investigated mixed oxides in comparison with pure MnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>. The population of the basic sites has been estimated from the area of the TPD profiles (see Supplementary Information). The MnO<sub>2</sub> presents preponderant strong basic sites, while Fe<sub>2</sub>O<sub>3</sub> is characterized by low and medium basic sites.

As revealed in **Fig. 3** and Table S1 (see Supplementary information), both the total number of basic sites and the base strength distribution are influenced by the Mn/Fe ratio: (i) sites of medium strengths were the most abundant in Mn 0.75/Fe 0.25 mixed oxides, (ii) the total number of basic sites decreased when the amount of the manganese cations lowered from 1.84 mmol/g in Mn 0.75/Fe 0.25 to 0.92 mmol/g in Mn 0.5/Fe 0.5 sample. Additionally, according to **Fig. 3** the increase of the Mn content generates a higher number of medium strength basic sites, which are not detected in pure oxides. This suggests the existence of a synergy between the two phases in the mixed oxide and is consistent with the higher total number of basic sites in mixed oxides compared with pure oxides.

As described in **Table 3** and **Fig. 3**, the CO<sub>2</sub>-TPD results correlate very well with the catalytic performances of our materials, leading to the conclusion that the catalytic activity is merely associated with the presence of the medium strength basic sites as in the case of Mn 0.75/Fe 0.25. The role of the catalyst's basic sites (medium strength) represented mainly by O<sup>2-</sup> (Lewis type basicity) is to enhance the catalyst's oxidant activity, while the role of NaOH (Brönsted base) is to produce the Cannizzaro products, which

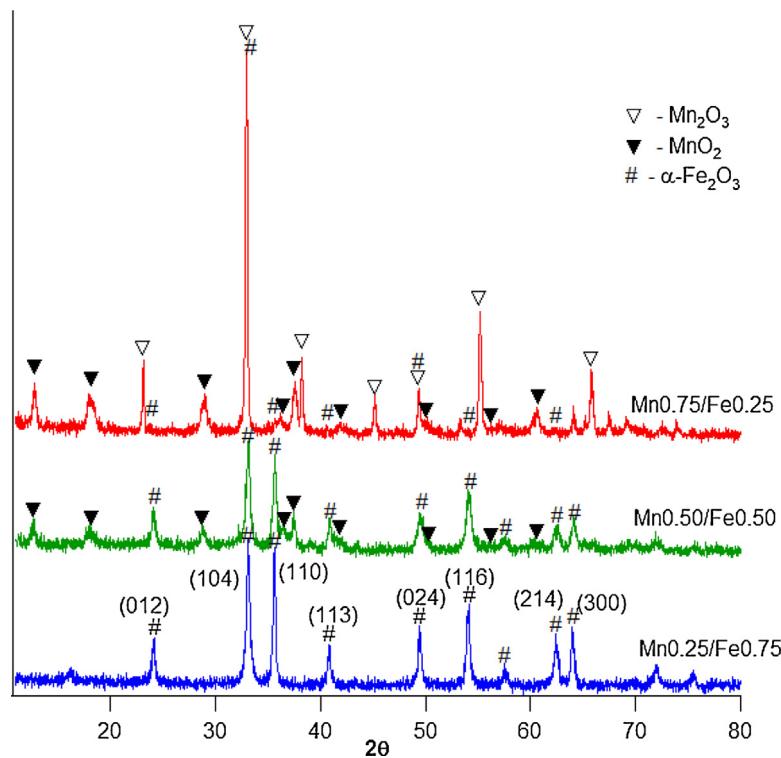


Fig. 2. XRD patterns of the  $\text{MnX/Fe(1-X)}$  mixed oxides.

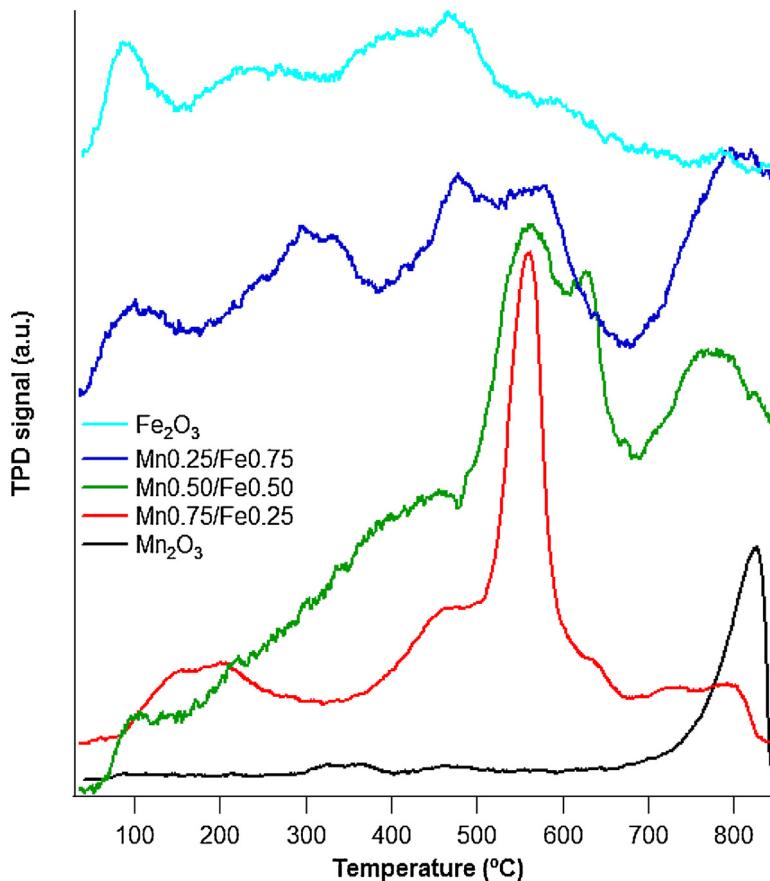


Fig. 3.  $\text{CO}_2$ -TPD profiles of the  $\text{Mn}_x\text{Fe}_y$  mixed oxide catalysts.

are intermediates for the oxidation reaction. **Scheme 2** depicts the suggested reaction pathways for the oxidation of HMF in the presence/or absence of the investigated catalysts.

#### 4. Conclusions

In summary, in the first step, the transformation of HMF in FFCA can be achieved only in the presence of NaOH and oxygen. The second step of the reaction, *i.e.*, the oxidation of FFCA to FDCA requires the presence of a catalyst. However, in the first step of reaction in the absence of catalyst, besides the desired products (FFCA), humins species are generated which can further deactivate the catalyst. To avoid this, the present contribution proposes a two steps procedure. First step is considering the oxidation of HMF to FFCA in the presence of a Brønsted base and oxygen. Optimization experiments revealed a molar ratio of HMF:NaOH of 1: 4 that generated better conversions and selectivities. Second step implies purification of FFCA at pH 1, where humins species are removed by a simple precipitation/filtration method. The oxidation of the purified FFCA to FDCA was then carried out using a non-precious metal catalyst, *i.e.*, a mixed Mn/Fe oxide. The optimal composition of this oxide corresponds to an atomic Mn/Fe ratio of 3/1 where a mixture of Mn(III) and Mn(IV) coexists with a hematite phase. The synergistic cooperation of these phases allowed the efficient oxidation of FFCA to FDCA under mild reaction conditions, in which both base and oxidation active sites played crucial roles.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2015.07.043>

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